Journal of Organometallic Chemistry xxx (2017) 1–9

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

NMR spectroscopic study of the adduct formation and reactivity of homoleptic rare earth amides with alkali metal benzyl compounds, and the crystal structures of $[Li(TMEDA)_2][Nd\{N(SiMe_3)_2\}_3(CH_2Ph)]$ and $[\{Li(TMP)\}_2\{Li(Ph)\}]_2$

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ARTICLE INFO

Article history:
Received 14 August 2017
Received in revised form
16 October 2017
Accepted 17 October 2017
Available online xxx

Keywords:
f-block organometallics
Metal amide
Bimetallic
Benzyl
Alkali-metal
Cyclometallate

ABSTRACT

An NMR spectroscopic study has been conducted into the reactivity of alkali metal benzyls $[M(CH_2Ph)]$, (M = Li, Na, K) with lanthanide tris(amide) complexes $[Ln(N'')_3]$ (Ln = Y, Ce, Nd; $N'' = N(SiMe_3)_2$) and $[Ce(TMP)_3]$ (TMP = 2,2,6,6-tetramethylpiperidide). It was found that for $[Ln(N'')_3]$, benzyl adducts $[M][Ln(N'')_3(CH_2Ph)]$ were initially formed, and the molecular structure for $M = Li(TMEDA)_2$ and Ln = Nd was determined revealing a distorted tetrahedral $[Nd(N'')_3(CH_2Ph)]$ anion. In all cases, these adduct complexes were unstable, intramolecularly deprotonating a methyl arm of a N″ ligand via benzyl basicity and eliminating toluene to prepare cyclometallated complexes of the form $[M][Ln(N'')_2\{\kappa^2\text{-}CH_2Si(Me)_2N(SiMe_3)\}]$. In parallel studies, reactions of $[Li(Ph)]$ with $[Ln(N'')_3]$ (Ln = Ce, Nd) afforded $[Li(N'')]$, whilst for (Ln = Y) adduct formation was observed. $[Ce(TMP)_3]$ did not generate any characterisable bimetallic adducts. The reaction of $[Li(Ph)]$ with $[Li(TMP)]$ afforded the hexanuclear $[\{Li(TMP)\}_2\{Li(\mu\text{-}Ph)\}]_2$, which features lithium in three different coordination environments.

1. Introduction

Research into mixed-metal organometallics has demonstrated that certain bi- and multi-metallic compounds have patterns of reactivity that can be both wider in scope and more selective than the individual components on their own [1]. This has led to the systematic development of mixed-metal compounds with synergic reactivity [2] that have many potential applications including selective metalation reactions [3] for more efficient organic synthesis [4], as well as for use in catalysis (*e.g.* mixed f-block/Mg polymerisation catalysts) [5,6]. One particularly well known example of enhanced reactivity of a bimetallic system is the widely used Lochmann-Schlosser base, which is a mixture of *n*-butyllithium and potassium *tert*-butoxide [3].

Alkali metal secondary amides – in particular $[M\{N(^iPr)_2\}]$, $[M\{N(SiMe_3)_2\}]$ and $[M(TMP)]$; M = Li, Na, K; TMP = 2,2,6,6-tetramethylpiperidide – are ubiquitous throughout synthetic chemistry [7], and their synergic behaviour with, for example, Mg, Mn and Zn organometallics leads to unusual reactivity that can be understood through detailed knowledge of the structure of these reagents (*e.g.* **I**, Fig. 1) [1,3]. Rare earth amides and organometallics, on the other hand, are not widely used throughout chemistry with their use mainly restricted to synthetic f-block chemistry [8]. Simple homoleptic starting materials, such as $[Ln(N'')_3]$ [9] and $[Ln\{CH(SiMe_3)_2\}_3]$ [10–12], and the THF solvated $[Ln(CH_2Ph)_3(THF)_n]$ (n = 2 [13,14] or 3 [13–16]) and $[Ln(CH_2SiMe_3)_3(THF)_n]$ (n = 2 [17,18] or 3 [17,19]), are well known, although they are very air- and moisture-sensitive and can be non-trivial to synthesise. The rare earth elements, with their large ionic radii, high coordination numbers and interactions dominated by ionic bonding, also have a well-developed ‘ate’ chemistry producing charge separated lanthanide complexes when additional anionic ligands bind to the Ln metal centres [20]. Examples of charge-separated organometallic lanthanide ‘ate’ compounds include $[Li(L)_n][LnR_4]$ {$R = {}^tBu$ [21–23], CH_2SiMe_3 [22,24,25]; $(L)_n = (THF)_4$, $(TMEDA)_2$, $(DME)_3$; $DME = MeOC_2H_4OMe$}, the heteroleptic $[Li(DME)_3][Nd(Cp)_3(Ph)]$

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https://doi.org/10.1016/j.jorganchem.2017.10.022
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Please cite this article in press as: S.G. Rachor, et al., Journal of Organometallic Chemistry (2017), https://doi.org/10.1016/j.jorganchem.2017.10.022

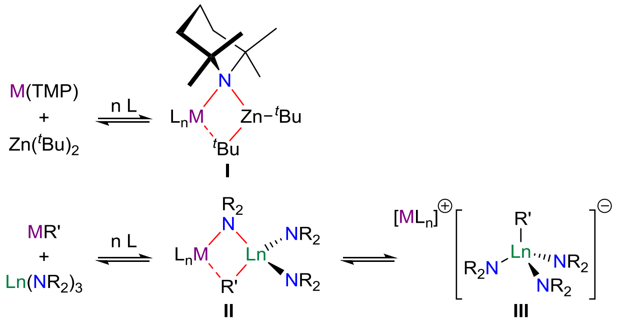


Fig. 1. Bimetallic mixed-metal organometallic compounds.

[26] and [Yb^{II}(CH$_2$Ph)(THF)$_5$][Yb^{III}(CH$_2$Ph)$_4$(THF)$_2$] which formed in preference to neutral [Yb^{III}(CH$_2$Ph)$_3$(THF)$_3$] [13]. Contacted ion-pairs are also known (Fig. 2, top), for example, with Me: [Ln{(μ-Me)$_2$Li(TMEDA)}$_3$] [27,28], N(^{i}Pr)$_2$: [Li(μ-N^{i}Pr$_2$)$_2$Y(N^{i}Pr$_2$)$_2$] [29], N″: [Li(μ-N″)$_2$Ln^{II}N″] [30] and CH$_2$Ph: [K(THF)K(THF)$_2$Sc(μ-CH$_2$Ph)$_5$], which contains a complicated extended structure in the solid state [15].

We were interested in lanthanide motifs with two different bridging atoms similar to **I**, because only a handful of structurally characterised examples are known (Fig. 2, bottom) that show lanthanide complexes with mixed alkyl/amide bridging interactions (type **II**, Fig. 1) [31–33]. These include cyclometallated complexes that result from N″ ligand deprotonation [34–36], such as [K][Y(N″)$_2${κ^2-CH$_2$Si(Me)$_2$*N*(SiMe$_3$)}] [30] that becomes a solvent separated ion pair when a co-ligand such as 18-crown-6 is used [37]. These cyclometallated structures demonstrate one potential drawback from using the ubiquitous N″ anion as a supporting ligand because group 1 organometallics are strong bases; [Na(N″)], [K{Si(SiMe$_3$)$_3$}] and ^{n}BuLi/TMEDA react with [Ln(N″)$_3$] (Ln = Y, Yb) to deprotonate the N″ ligand forming a dianionic (κ^2-N,C) ligand [30,34] instead of generating a stable bimetallic adduct. In contrast, the reaction of [Yb(N″)$_3$] with ^{t}BuLi caused reduction to Yb(II) and formation of [LiYb(N″)$_3$] [30].

Synergic reactivity based upon bimetallic complexes of group 1 and the rare earths has not been systematically investigated, so this paper details our first investigations in this field targeting bimetallic complex formation using weaker bases than butyl lithium (type **II**). We show that adducts are initially formed, which can be stable for several days, long enough to crystallise a heteroleptic Nd 'ate' species (type **III**, Fig. 1).

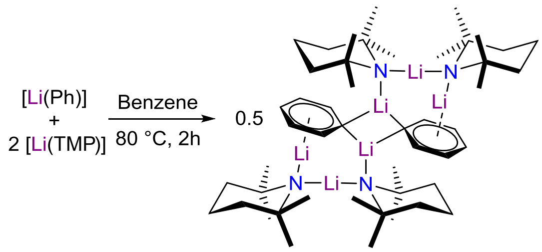
2. Results and discussion

2.1. Homometallic species

Initially, we investigated the reaction of a lithium organometallic with a lithium amide in order to study adduct formation using the same very electropositive metal (Pauling electronegativity, χ_P, of Li = 0.98) [38]. This would allow us to investigate ligand compatibility and bonding modes that could then be applicable to heterobimetallic systems including rare earth elements.

The 1:1 reaction of [Li(Ph)] with [Li(TMP)] in benzene at 80 °C for 2 h afforded a brown suspension, wherein only some of the lithium phenyl was observed to dissolve. Upon cooling, pale yellow crystals suitable for X-ray diffraction studies were grown, which revealed this complex to be the hexanuclear species [{Li(TMP)}$_2${Li(μ-Ph)}]$_2$, (**1**). Repeating the reaction with a 1:2 ratio of [Li(Ph)]:[Li(TMP)] (Scheme 1) resulted in a clear solution from which the same product crystallised upon cooling in improved yield (37%). Both triclinic ($P\bar{1}$) and monoclinic ($P2_1/n$) polymorphs have been characterised, with virtually identical molecular structures.

Compound **1** is a hexanuclear centrosymmetric complex (see Fig. 3), containing six lithium atoms in three different coordination geometries. The first environment is the η^1:η^1-Li(1), which is bound to the amide nitrogen atoms of two TMP molecules. Although this is formally only two-coordinate at lithium, the flanking methyl groups of the TMP ligand must provide some degree of steric protection, as is true of the tetrameric lithium reagent [{Li(TMP)}$_4$],



Scheme 1. Preparation of [{Li(TMP)}$_2${Li(μ-Ph)}]$_2$ (**1**).

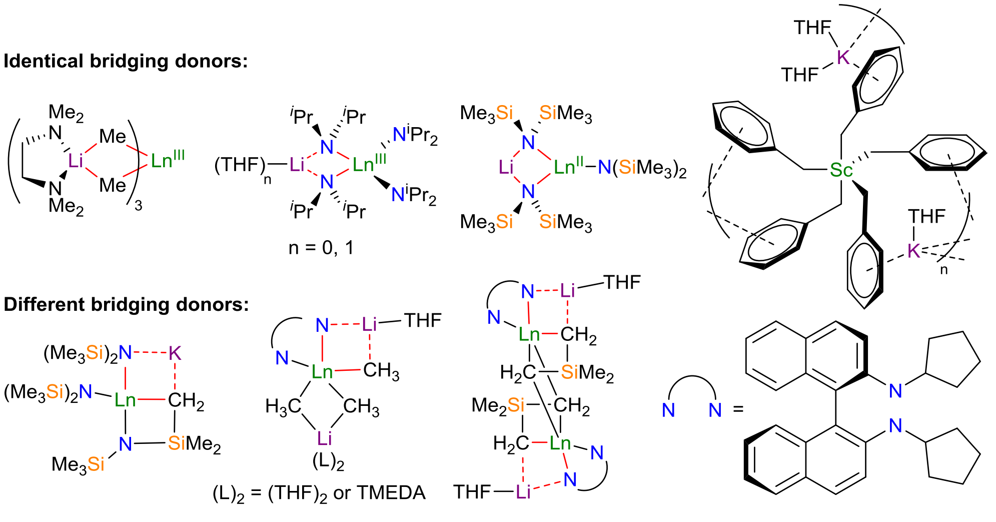


Fig. 2. Organometallic lanthanide contacted ion pairs.

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